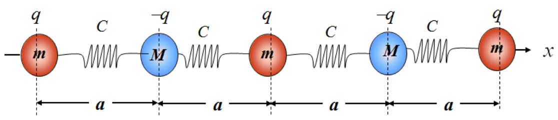
# THERMAL PROPERTIES

# *Overview: Lecture 6*

- Optical Excitation:

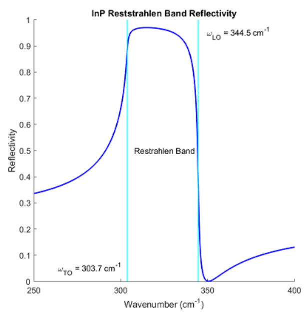



- Equations of motions
  → Resonance:

$$u_{2n} = \frac{-qE_0 / m}{\omega_0^2 - \omega_+^2(0)} e^{-i\omega_0 t}$$

$$u_{2n+1} = \frac{qE_0 / M}{\omega_0^2 - \omega_+^2(0)} e^{-i\omega_0 t}$$

- Reststrahlen effect and band

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## *Overview: This Lecture*

- Phonon vs. photon
- Specific heat
  - Classical theory
  - Einstein's theory

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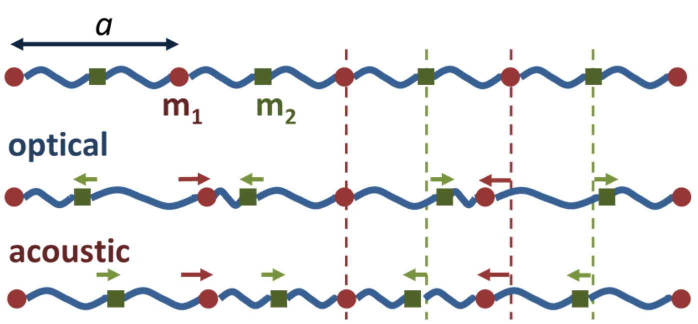
## *Phonon*

- Collective excitation of periodic atoms.
- Quasi particle with a momentum and a quantized energy.

$$p = \hbar k,\ E = \hbar\omega$$

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## *Phonons Vs. Photons*

**PHONONS**

- Quanta of lattice vibrations
- Energies of phonons are quantized

**PHOTONS**

- Quanta of electromagnetic radiation
- Energies of photons are quantized as well

$$E_{\text{phonon}} = \frac{h\nu_s}{\lambda}$$

$\lambda$: $\sim a_0 = 10^{-10}$ m

$$p_{\text{phonon}} = \frac{h}{\lambda}$$

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

$\lambda$: $\sim 10^{-6}$ m

$$p_{\text{photon}} = \frac{h}{\lambda}$$

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## *Specific Heat*

- The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius.
- $dQ$: Applied heat $\rightarrow$ $dQ = dE + p\,dv$
- $dE$: Internal energy, $pdv$: External work
- Specific heat: $\dfrac{dQ}{dT} = \dfrac{dE}{dT} + \dfrac{d(p\,dv)}{dT}$
- At constant volume and pressure:

$$c_v = \left.\frac{dQ}{dT}\right|_v = \frac{dE}{dT} \qquad c_p = \left.\frac{dQ}{dT}\right|_p = \frac{dE}{dT} + p\frac{d(dv)}{dT}$$

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# Specific Heat

- In solids: $c = c_p = c_v = \dfrac{dE}{dT}$
- What is the significance of specific heat of a substance?
- What is the specific heat of water?

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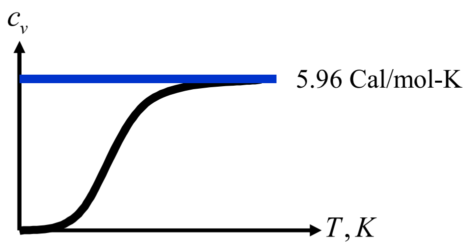
# Classical Theory

- **Law of Dulong and Petit:** An empirical finding that the specific heat of most solid substances at and above room temperature is independent of temperature → 5.96 cal/mol-K.
- At $T$ far below room temperature the behavior is very different.

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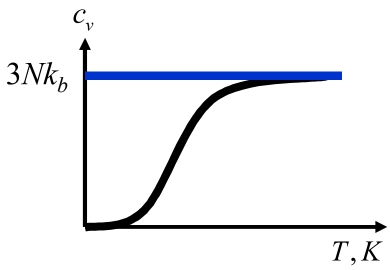
# *Classical Model*

- $N$ independent three-dimensional simple harmonic oscillators → $3N$ one-dimensional oscillators.
- Total internal energy:

$$U = 3Nk_bT$$

- Specific heat: $c_v = \frac{\partial U}{\partial T} = 3Nk_b$




- Assumptions:
  - Quantum effects are completely ignored.
  - Oscillators are assumed to vibrate at a single frequency.

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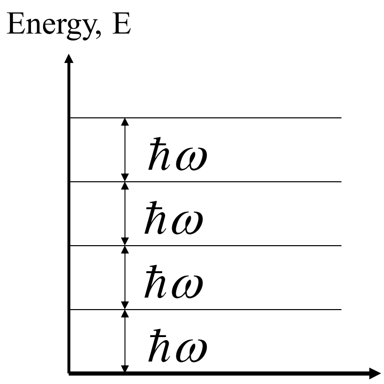
# *Einstein's Theory*

**Harmonic oscillators:**

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$n = 0, 1, 2, 3, \dots$$




- The discrepancies are due to quantum effects.
- $3N$ uncoupled one-dimensional harmonic oscillators.
- Energies are restricted to discrete values.
- Atoms are vibrating at a single frequency.

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## Harmonic Oscillators

It is possible to consider $\varepsilon_n$ as constructed by adding $n$ excitation quanta each of energy $\hbar\omega$ to the ground state.

$$\varepsilon_0 = \frac{1}{2}\hbar\omega$$

A transition from a lower energy level to a higher energy level.

$$\Delta\varepsilon = \left(n_2 + \frac{1}{2}\right)\hbar\omega - \left(n_1 + \frac{1}{2}\right)\hbar\omega$$

$$\Delta\varepsilon = \underbrace{\left(n_2 - n_1\right)}_{unity}\hbar\omega \Rightarrow \Delta\varepsilon = \hbar\omega$$

*absorption of phonon*

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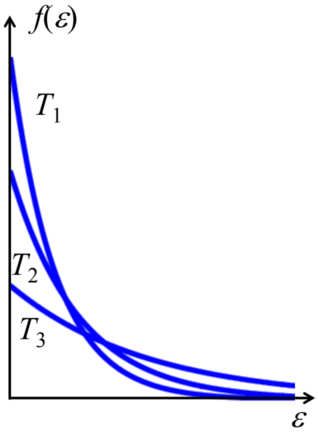
## Maxwell-Boltzmann Distribution

- Identifiable system of identical particles.
- Pauli's exclusion principle does not apply.
- Total energy is constant.

$$f(\varepsilon) = e^{\alpha} e^{-\varepsilon/k_b T}$$

- $k_b$: Boltzmann's constant
- $T$ : Absolute temperature

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# *Internal Energy*

- $N$ independent three-dimensional simple harmonic oscillators → $3N$ one-dimensional oscillators.
- We can calculate the total internal vibrational energy.

$$\frac{U}{N} = \frac{\int_0^\infty \varepsilon N(\varepsilon) d\varepsilon}{\int_0^\infty N(\varepsilon) d\varepsilon} = \frac{\int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon}{\int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon}$$

- $f(\varepsilon)$: Distribution function
- $g(\varepsilon)$: Density of states



# *Mean Energy*

- Integrals are replaced by summations and density of states by degeneracy of widely spaced levels

$$\langle \varepsilon \rangle = \frac{\sum_{n=0}^{\infty} \varepsilon_n g_n e^{\alpha} e^{-\varepsilon_n / k_b T}}{\sum_{n=0}^{\infty} g_n e^{\alpha} e^{-\varepsilon_n / k_b T}} = \hbar\omega \frac{\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) e^{\left(n+\frac{1}{2}\right)x}}{\sum_{n=0}^{\infty} e^{\left(n+\frac{1}{2}\right)x}}$$

- where $x = -\hbar\omega / k_b T$
- $g_n = 1$

# Mean Energy

$$\langle \varepsilon \rangle = \hbar\omega \frac{\frac{1}{2}e^{\frac{1}{2}x} + \frac{3}{2}e^{\frac{3}{2}x} + \frac{5}{2}e^{\frac{5}{2}x} + \cdots}{e^{\frac{1}{2}x} + e^{\frac{3}{2}x} + e^{\frac{5}{2}x} + \cdots}$$

$$= \hbar\omega \frac{d}{dx} \ln\left[ e^{\frac{1}{2}x}\left(1 + e^{x} + e^{2x} + \cdots\right)\right]$$

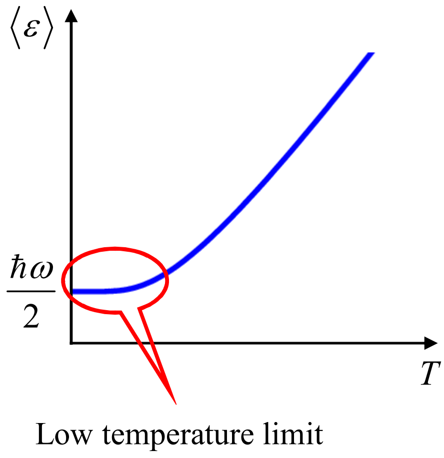
$$= \hbar\omega \frac{d}{dx}\left[\frac{1}{2}x - \ln\left(1 - e^{x}\right)\right] = \hbar\omega\left[\frac{1}{2} + \frac{e^{x}}{1 - e^{x}}\right]$$

$$= \hbar\omega\left[\frac{1}{2} + \frac{1}{e^{-x} - 1}\right] = \hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_bT} - 1}\right]$$



# Mean Energy

$$\langle \varepsilon \rangle = \hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_bT} - 1}\right]$$

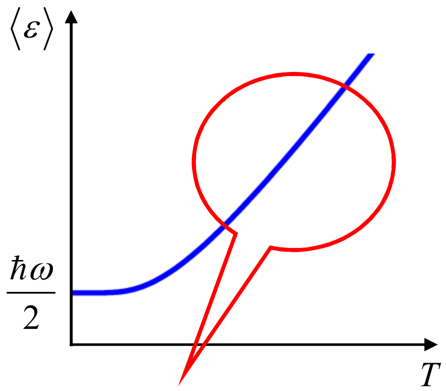



$$\hbar\omega \gg k_bT$$

$$\langle \varepsilon \rangle \approx \frac{\hbar\omega}{2}$$

# Mean Energy

$$\langle \varepsilon \rangle = \hbar\omega \left[ \frac{1}{2} + \frac{1}{e^{\hbar\omega/k_bT} - 1} \right]$$




High temperature limit

$\hbar\omega \ll k_bT$

$$\langle \varepsilon \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{1 + \frac{\hbar\omega}{k_bT} - 1}$$

$$= \frac{\hbar\omega}{2} + k_bT \approx k_bT$$

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# Specific Heat: Einstein Model

- Internal energy:

$$U = 3N\langle \varepsilon \rangle = \frac{3N\hbar\omega}{2} + \frac{3N\hbar\omega}{e^{\hbar\omega/k_bT} - 1}$$

Zero-point energy

Temperature-dependent → contributes to specific heat

- Specific heat:

$$c_v = \left( \frac{\partial U}{\partial T} \right)_v = 3N\hbar\omega \frac{-1}{\left(e^{\hbar\omega/k_bT} - 1\right)^2} e^{\frac{\hbar\omega}{k_bT}} \frac{-\hbar\omega}{k_bT^2}$$

$$= 3Nk_b \left( \frac{\hbar\omega}{k_bT} \right)^2 \frac{e^{\hbar\omega/k_bT}}{\left(e^{\hbar\omega/k_bT} - 1\right)^2}$$

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## *Specific Heat: Einstein Model*

- Einstein temperature:

$$\hbar\omega = k_b \Theta_E$$

- Specific heat:

$$c_v = 3Nk_b \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{\left(e^{\Theta_E/T} - 1\right)^2}$$

- At Einstein temperature, $\Theta_E / T = 1$, $c_v = 0.921 \times 3N k_b$.
- Above $\Theta_E$, classical theory is relatively accurate.
- Below $\Theta_E$, quantum effects become increasingly significant.

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## $T \rightarrow 0$

$$c_v = 3Nk_b \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{\left(e^{\Theta_E/T} - 1\right)^2}$$

$$c_v = 3Nk_b \left(\frac{\Theta_E}{T}\right)^2 \frac{1}{e^{\Theta_E/T} - 2 + e^{-\Theta_E/T}}$$

$$T \downarrow \quad e^{\Theta_E/T} \uparrow \quad c_v \downarrow$$

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## $T \rightarrow \infty$

$$c_v = 3Nk_b \left(\frac{\Theta_E}{T}\right)^2 \frac{1}{e^{\Theta_E/T} - 2 + e^{-\Theta_E/T}}$$

$$c_v = 3Nk_b \left(\frac{\Theta_E}{T}\right)^2 \frac{1}{1 + \frac{\Theta_E}{T} + \frac{1}{2}\left(\frac{\Theta_E}{T}\right)^2 - 2 + 1 - \frac{\Theta_E}{T} + \frac{1}{2}\left(\frac{\Theta_E}{T}\right)^2}$$

$$= 3Nk_b \left(\frac{\Theta_E}{T}\right)^2 \frac{1}{\left(\frac{\Theta_E}{T}\right)^2} = 3Nk_b$$

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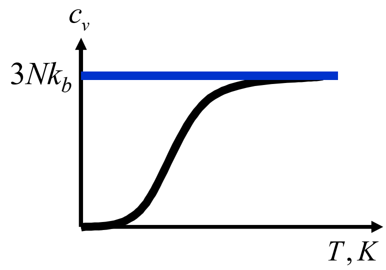
## *Discrepancies*

- Einstein's theory: exponential temperature dependence
- Experiment: $T^3$ temperature dependence.
- **Limitations:** Independent oscillators and single frequency.
- **MUST** include vibrational frequency spectrum with dispersion relation and the quantization of the oscillator energies.

→ **Debye Theory**

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